Propargyl Bromide - A Possible Chemical Alternative to Methyl Bromide for Pre-Plant Soil Fumigation

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Propargyl bromide (3-bromopropyne, C3H3Br or 3BP) was used in the 1960's in a soil fumigant called Trizone, a combination of chloropicrin, methyl bromide (MeBr) and propargyl bromide. At present, however, no information exists on 3BP's behavior and safety in the environment. In this study, several important parameters needed to determine its environmental fate are obtained and include: solubility, saturated vapor density, the Henry's law constant, adsorption and degradation

Solubility. A chemical's solubility is an important parameter affecting how rapidly a chemical will move through porous media. At low temperatures (2-20°C), the solubility increases rapidly as temperature rises and levels off at approximately 25-30 °C. At 25°C, the 3BP solubility is 14,900 mg/L or approximately 1.5% and is comparable to MeBr (13,400 mg/L). The solubility of 1,3-D in water is much less than 3BP with values at 25°C from 2320 mg/L (trans- 1,3-D) and 2180 mg/L (cis- 1,3-D). Therefore, under conditions of high leaching, a larger fraction of 3BP will move with the water.

Saturated Vapor Density. The vapor density gives an indication of the volatility of a chemical. Generally, all the agricultural fumigants have a high vapor density since it is desirable to rapidly move the chemical throughout the soil. At 25 °C the saturated vapor density, $p_{v,sat}$ is approximately 388 mg/L and is greater than the estimated $p_{v,sat}$. for 1,3-D (i.e., 205 mg/L (cis) and 137 mg/L (trans)) at 25 °C. Both 3BP and 1,3-D have lower saturated vapor density compared to MeBr ($p_{v,sat} \approx$ 3 878 mg/L).

Hydrolysis in Water and Degradation in Soil. 3BP slowly degrades in water and has a half-life of approximately 47 days. This value is similar to the measured $t_{1/2}$ for MeBr hydrolysis in water which is 20-50 days, and the longer reported $t_{1/2}$ for 1,3-D hydrolysis which is 51 days for a temperature of 10 °C.

The degradation of 3BP in three soils was determined by measuring changes in the residual concentration with time. The degradation kinetics were well described using a first-order model (Table 1). In the same soil, 3BP degrades at a similar rate as 1,3-D but much faster that MeBr. The calculated $t_{1/2}$ for MeBr would be 3-6 times that for 3BP in the same soil. In the Greenfield sandy loam, a $t_{1/2}$ as long as 22 d was obtained for MeBr whereas, in Arlington sandy loam (very similar to Greenfield sandy loam), the $t_{1/2}$ for 3BP was approximately 3 days. Since 3BP degrades rapidly in soil, it will likely result, in lower volatilization and limited downward movement compared to MeBr.

Henry's Law Constant, K_H. The partition of a chemical between air and water is extremely important in determining how easily a chemical moves in soils and the fraction of chemical that enters the atmosphere through volatilization. At 25 °C, the K_h, was found to be 0.046 and nearly doubled to 0.080 at 40°C. This K_H value for 3BP is approximately the same as that for 1,3-D and is about 5 times smaller than the value for MeBr *(K_H =0.24 to 0.3 at 20°C).* With a K_H of 0.046 at 25 °C, the movement of 3BP in soil can also be expected to be dominated by gas-phase diffusion but should be at a rate slower than MeBr.

Adsorption. The measured K_d values for 3BP on these soils ranged from 0.07 to 0.39 cm^3/gm. After correcting for degradation during the equilibrium period, the amount adsorbed on the Carsitas soil was within the range of experimental errors, and K_d becomes negligible. For Arlington and Linne soils, small adsorption parameters remain. After correction for degradation, K_d for 3BP on the tested soils ranged from 0 to 0.049 cm^3/grn. This compares to values less than 0. 1 cm^3/g for MeBr and between 1.3 to 1.5 cm^3/g for 1,3-D.

Behavior in Soil. Several mobility indices were computed to determine how 3BP will behave in soil, including: the retardation and attenuation factors and the convective and diffusive mobility times. The retardation factor (RF = 1 +(K_d p_b/0 + a K_H/0*)* is an index of the relative time needed for a pesticide to move past some specified depth, compared to a non-adsorbing tracer, where p_b, 0 and *a* are, respectively, the bulk density, water content and air content. The attenuation factor (AF = Exp[-k 0 RF l/q]) i*s* the fraction of pesticide mass that is likely to move past some specified depth, l, given some specified recharge rate, *q*. This index includes the effects from adsorption, *RF*, and degradation, k. The convective and diffusive mobility times give a measure of the time needed for a pesticide to travel a distance, l, by convection, $t_c = (0 + K_d p_b + a K_H)l/q$, or diffusion, $t_D = l^2 Q^2(0 + K_d p_b + a K_H)/(D^a_g a^{3\ 1/3} K_H)$. A summary of these indices is given in Table 2 for 3BP, MeBr, 1,3-D and a few other common pesticides.

The RF is a measure of the effect of adsorption (e.g., atrazine, carbaryl and lindane) and vapor partitioning (e.g., fumigants on a pesticide's mobility. The RF for all the fumigants range from 1.2 to 2.8, and are less than the other commonly used pesticides listed in Table 2. Therefore, the RF indicates that all of the fumigants will be transported at a slower rate compared to a conservative tracer, even though their adsorption coefficients are nearly zero. The AF, which includes the effects of degradation, indicates that approximately 18% of the 3BP will travel 25 cm compared to 59% of the MeBr, an amount that is 3 times less. If the travel distance is extended to 50 cm, only 3% of the 3BP remains compared to 34% for MeBr. The attenuation of 3BP is somewhat less than 1,3-D which ranges from 2 to 4% after traveling 25 cm.

The effect of convection and diffusion on the movement of 3BP and the other fumigants in soil may be seen from the behavior of the convective and diffusive mobility times, t_c, t_D. In this example, the transport distance and flux density are 10 cm and I cm/day. Using the classification scheme (Jury et al., 1984), it is found that 1) all the fumigants have high convective mobility, 2) 3BP and MeBr have high diffusive mobility, 3) 1,3-D ranges from high to moderate diffusive mobility and 4) MITC has moderate diffusive mobility. Since diffusive mobility is the principal reason fumigants are rapidly transported in soil, pesticides with low diffusive mobility may suffer from difficulties achieving a uniform soil concentration throughout the treatment zone. This has been observed in field studies using MITC to control root gall in tomatoes and strawberries and has caused others to develop better methods for distributing MITC. Due to its relatively high diffusive mobility and low retention on soils, 3BP should readily move through the soil and provide a reasonably uniform concentration distribution. Also, as indicated by its AF, 3BP possesses the desirable trait of high degradation. This will help limit the amount of applied chemical that reaches the atmosphere or ground water after application, compared to MeBr.

Table 1. First-order Degradation Rate Constants (d^{-1}) for 3-Bromopropyne (C_3H_3Br), Methyl Bromide (CH_3Br) and 1,3-D in California Soils.

Soil	3BP	Methyl Bromide	cis-1,3-D	trans-1,3-D
Arlington sandy loam	0.18	0.03	0.15	0.19
Carsitas loamy sand	0.57	0.12		
Linne clay loam	0.39	0.12		

r^2 were greater than 0.95 for all degradation rate constants.

Table 2 Mobility indices for selected pesticides

Pesticide	RF[a]	AP[a]	t_c[a] l = 25 cm	t_D[a] l = 10 cm	Class[b] l =10 cm
3BP	1.25	0.18	3.75	11.54	3
MeBr	2.37	0.59	7.12	4.03	3
1,3-D(Z)	2.81	0.042	8.44	16.19	3
1,3-E)(E)	2.79	0.019	8.38	27.60	2
MI TC	1.34	0.37	4.01	55.18	2
2,4-D	2.10	0.33	6.31	§	I
atrazine	6.52	0.56	19.62	§	I
carbaryl	17.6	0.0001	52.69	§	I
lindane	61.7	0.45	185.19	§	I

§ indicates greater than 10^5

[a]- RF, AF, t_c and t_D indicate, respeclively, retardation factor, attenuation factor, convective mobility time and diffusive mobility time.

[b] - classification scheme of Jury et al. (1984) with larger numbers indicating high mobility